

II. "On the Molecular Heat and Volume of the Rare Earths and their Sulphates." By L. F. NILSON and OTTO PETTERSSON. Communicated by WARREN DE LA RUE, D.C.L., F.R.S. Received June 21, 1880.

At the request of the Royal Academy of Sciences at Stockholm, we some years ago undertook an extended research into the physical properties of the rare earth-metals and their compounds. Having performed the laborious task of separating and purifying their oxides, we are now able to publish our first series of determinations concerning their principal properties, which chemically are of the greatest importance, viz., molecular heat and molecular volume.

The rare earths, with a few exceptions (CeO_2 , ThO_2 , ZrO_2), belong to a group of sesquioxides. In order to obtain a larger number for comparison, we have extended our research not only to the rare earths, but also to some other nearly related compounds, the molecular heat and volume of which were hitherto unknown. As to these values, previously known for some other oxides, Al_2O_3 , Fe_2O_3 , Cr_2O_3 , according to Regnault, Kopp, and others, we have already observed in our preceding paper "On the Essential Properties and Chemical Character of Beryllium," that only such determinations are strictly comparable which are made by the same method, under the same circumstances, and referred to the same unit of measure.

The specific densities and molecular volumes, which are given in the following tables, are obtained by means of a method, specially adapted to prevent the errors arising from adhesion of air to pulverulent substances.* The densities taken by this method will therefore generally be found a little higher and the molecular volumes a little lower than the numbers usually given by others.

The specific heats of the different compounds are determined with Bunsen's ice-calorimeter, by means of the same process which we have more fully described in our detailed memoir on beryllium.† All the numbers given are the means of at least two determinations, which agree perfectly, the experiments being made under the most favourable circumstances. As to the values obtained, we beg to observe that the specific and molecular heat will be found a little smaller by the ice-melting method than by other methods, on account of the different unit of comparison.

The molecular weight of the different oxides was determined by a special analysis or synthesis of the sulphates, and the very same chemi-

* For the details, see Otto Pettersson, "Molecularr volumina einiger Reihen von isomorphen Salzen," in "Nov. Act. reg. Soc. Scient. Ups.," ser. iii. Upsala, 1873.

† "Pogg. Ann.," [2], iv, p. 554.

cally pure substances were employed both for the thermic, volumetric, and magnetic experiments. The results only and not the details of these experiments are given in the tables.

Oxides.

Compounds.	Formula.	Molecular weight.	Specific weight.	Specific heat.	Molecular heat.	Molecular volume.
Beryllium oxide ..	Be_2O_3 ...	75·3	3·016	0·2471	18·61	24·97
Aluminium oxide..	Al_2O_3	102·8	3·990	0·1827	18·78	25·76
Sapphire cryst....	Al_2O_3	102·8	3·990	0·1879	19·32	25·76
Chrysoberyl cryst..	$\left. \begin{matrix} \text{Al}_2\text{O}_3 \\ \text{Be}_3 \end{matrix} \right\} \text{O}_3$..	95·9	3·734	0·2004	19·22	25·69
Scandium oxide*..	Sc_2O_3	136·0	3·864	0·1530	20·81	35·19
Gallium oxide† ...	Ga_2O_3 ...	184·0	—	0·1060	19·50	—
Yttrium oxide	Y_2O_3	227·0	5·046	0·1026	23·29	44·99
Indium oxide.....	In_2O_3	274·8	7·179	0·0807	22·17	38·28
Erbium oxide‡....	Er_2O_3 ...	380·0	8·640	0·0650	24·70	43·98
Ytterbium oxide ..	Yb_2O_3 ...	394·0	9·175	0·0646	25·45	42·94
Lanthanum oxide .	La_2O_3	326·0	6·480	0·0749	24·42	50·31
Didymium oxide..	Di_2O_3	341·0	6·950	0·0810	27·62	49·07
Zirconium oxide...	ZrO_2	122·0	5·850	0·1076	13·13	20·86
Cerium bioxide ...	CeO_2	171·5	6·739	0·0877	15·04	25·45
Thorium oxide....	ThO_2	264·0	9·861	0·0548	14·47	26·77

Hitherto it was supposed to be a general rule, that the atomic heat of oxygen in any oxide was not less than 3·5 or greater than 5·1. The numbers above given compel us, however, to assign a still lower value to the atomic heat of oxygen in alumina and beryllia, viz., 2·34.§ Into these oxides it enters with a minimum capacity of heat and volume. From these earths upwards the molecular heat and volume of the sesquioxides gradually increase with increasing molecular weights.

The following table shows that the molecular heat (1) of Er_2O_3 , Yb_2O_3 , La_2O_3 , and Di_2O_3 nearly agrees with those for other sesquioxides, determined by Regnault; (2) that of Be_2O_3 , approaches to the same for alumina; and (3) that of ZrO_2 , CeO_2 , and ThO_2 is as high as the values for SnO_2 , TiO_2 , and zircon, determined by the same author, and for MnO_2 according to Kopp. The validity of Neumann's law receives hereby a new confirmation.

* According to Nilson.

† For the oxide employed we are under obligation to M. Lecoq de Boisaudran, who placed 0·138 grm. gallium at our disposal.

‡ Professor Cleve has kindly placed at our disposal the purest erbia he has been able to obtain.

§ See the preceding paper, page 41.

Formula.	Molecular weight.	Specific heat.	Molecular heat.	Authority.
Bo_2O_3	69·8	0·2374	16·57	Regnault
Cr_2O_3	152·4	0·1796	27·37	„
Fe_2O_3	160·0	0·1681	26·90	„
As_2O_3	198·0	0·1279	25·32	„
Sb_2O_3	292·0	0·0901	26·31	„
Bi_2O_3	468·0	0·0605	28·31	„
TiO_2	82·0	0·1703	13·97	„
$\left. \begin{matrix} \text{Si}_2 \\ \text{Zr}_2 \end{matrix} \right\} \text{O}_2$	90·8	0·1456	13·22	„
SnO_2	150·0	0·0933	14·00	„
MnO_2	87·0	0·1590	13·83	H. Kopp

Anhydrous Sulphates.

Compounds.	Formula.	Molecular weight.	Specific weight.	Specific heat.	Molecular heat.	Molecular volume.
Beryllium sulphate...	Be_2SO_4	315·3	2·443	0·1978	62·37	129·07
Aluminium sulphate..	Al_2SO_4	342·8	2·710	0·1855	63·59	126·50
Scandium sulphate...	Sc_2SO_4	376·0	2·579	0·1639	62·42	145·80
Chromium sulphate ..	Cr_2SO_4	392·4	3·012	0·1718	67·41	130·27
Ferric sulphate	Fe_2SO_4	400·0	3·097	0·1656	66·24	129·16
Gallium sulphate.....	Ga_2SO_4	424·0	—	0·1460	61·90	—
Yttrium sulphate	Y_2SO_4	467·0	2·612	0·1319	61·60	178·80
Indium sulphate	In_2SO_4	514·8	3·438	0·1290	66·41	149·77
Lanthanum sulphate..	La_2SO_4	566·0	3·600	0·1182	66·90	157·22
Cerium sulphate	Ce_2SO_4	567·0	3·912	0·1168	66·23	144·94
Didymium sulphate ..	Di_2SO_4	581·0	3·735	0·1187	68·96	155·55
Erbium sulphate	Er_2SO_4	620·0	3·678	0·1040	64·48	168·57
Ytterbium sulphate...	Yb_2SO_3	634·0	3·793	0·1039	65·87	167·15
Thorium sulphate	Th_2SO_4	424·0	—	0·0972	41·21	—

The molecular heat of the anhydrous sulphates of the sesquioxides varies only within very narrow limits; 61·60—68·96 for yttrium and didymium sulphate. The values for the salts of chromium, iron, indium, lanthanum, cerium, and didymium are nearly identical; whilst even the values of the remainder approach each other very nearly.

As the following hydrated sulphates are decomposed when heated to 100° , their capacity of heat was determined between 0° and 46° in the vapour of boiling CS_2 ; the beryllium sulphate not bearing even that temperature without losing water, its molecular heat could not be ascertained.

Hydrated Sulphates.

Compounds.	Formula.	Molecular weight.	Specific weight.	Specific heat.	Molecular heat.	Molecular volume.
Beryllium sulphate.	$\text{Be}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$	531.3	1.713	—	—	310.17
Yttrium sulphate.	$\text{Y}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$	611.0	2.540	0.2257	137.91	240.55
Lanthanum sulphate	$\text{La}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$	728.0	2.853	0.2083	151.64	255.17
Cerium sulphate	$\text{Ce}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$	657.0	3.220	0.1999	131.33	204.04
Didymium sulphate	$\text{Dy}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$	725.0	2.878	0.1948	141.23	251.91
Erbium sulphate*	$\text{Er}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$	764.0	3.180	0.1808	138.13	240.25
Ytterbium sulphate†....	$\text{Yb}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$	778.0	3.286	0.1788	139.11	236.79

On subtracting the values obtained for the anhydrous salts from the same numbers of the hydrated sulphates, we obtain a remainder expressing the molecular heat and volume of the water in combination. Thus the following values are obtained :—

Compounds.	Water in combination.	Molecular heat.	Molecular volume.
Ytterbium sulphate...	$8\text{H}_2\text{O}$	9.15	8.70
Erbium sulphate.....	$8\text{H}_2\text{O}$	9.21	8.96
Yttrium sulphate.....	$8\text{H}_2\text{O}$	9.54	7.72
Didymium sulphate ..	$8\text{H}_2\text{O}$	9.03	12.04
Lanthanum sulphate .	$9\text{H}_2\text{O}$	9.42	10.88
Cerium sulphate	$5\text{H}_2\text{O}$	13.02	11.82

The molecular heat and volume of free water being =18, it will be seen that by entering into combination with the sulphates of the rare earth-metals, its heat and volume are reduced in an extraordinary degree. In fact, the molecular heat and volume of water in these salts descends to a minimum value hitherto unknown.

Comparing the values given above, we readily find that in those groups of compounds intimately connected by isomorphism, the molecular heat of the compounds increases and the molecular volume decreases with increasing molecular weight of the compound or atomic weight of the element. This will be shown by the following table, in which the different isomorphous compounds, partly of yttrium, erbium, and ytterbium, partly of lanthanum and didymium, are brought into comparison :—

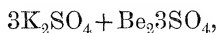
* According to Cleve.

† According to Nilson.

Elements.	Atomic weight.	Oxides.		Anhydrous sulphates.		Hydrated sulphates.	
		Molecular heat.	Molecular volume.	Molecular heat.	Molecular volume.	Molecular heat.	Molecular volume.
Yttrium	89.5	23.29	44.99	61.60	178.80	137.91	240.55
Erbium	166.0	24.70	43.98	64.48	168.57	138.13	240.25
Ytterbium	173.0	25.45	42.94	65.87	167.15	139.11	236.79
Lanthanum.....	139.0	24.42	50.31	66.90	157.22	—	—
Didymium	146.5	27.62	49.07	68.96	155.55	—	—

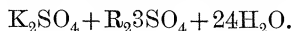
Especially with regard to beryllia, and the question of its real composition, the values given above are of the greatest importance. In respect of this we observe that: 1st, the atomic heat of oxygen in beryllia is identical with that in alumina and nearly identical with the same value in other closely related oxides, if beryllia = Be_2O_3 (see our preceding paper, p. 42); 2nd, under the same supposition the molecular heat and volume of beryllia and alumina are nearly identical, whether the latter earth be examined in the state of crystallised sapphire or of an amorphous powder, and, further, if we consider chrysoberyl not as an aluminate, but as $\left. \begin{smallmatrix} \text{Al}_3 \\ \text{Be}_3 \end{smallmatrix} \right\} \text{O}_3$, this mineral has yielded identical values; 3rd, the molecular heat and value of beryllium sulphate, compared with the same values for the other nearly allied sulphates of aluminium, scandium, gallium, and yttrium, support the formula Be_2O_3 which we have given.

Taking into consideration the above-mentioned circumstances, and those related in our former papers, with the fact that the atomic heat and volume of metallic beryllium, as well as the molecular heat and volume of beryllia and its sulphate, would assume values quite exceptional, if the formula for the oxide were BeO , we think, therefore, the question of the valence of beryllium may be considered as finally decided. In fact, there is no physical property of beryllium, beryllia, or its sulphates, which does not testify to our view being the correct one, and from a chemical point of view the same holds good. It is, we think, unnecessary to take up space here with a repetition of the various reasons which support this conclusion. We refer, therefore, to our detailed paper on beryllium, above quoted, and only mention here that this metal belongs on account of its sulphate,



to the series of the gadolinite and cerite metals, this salt having a composition, typical for all the members of this series (Be, Sc, Y, La, Ce, Di, Tr, Y_a , Y_β , α , Er, Tm, Yb). The series of these elements, the

leading member of which beryllium unquestionably is, stands certainly in the nearest proximity with an other series, that of aluminium (Al_3 , Ga_3 , Tn_3 , Cr_3 , Mn_3 , Fe_3), but this nevertheless decidedly differs from the former by an other typical double sulphate,



or alum.

The fact, which has been alleged as a proof of the bivalence of beryllium, namely, that the chloride fuses and sublimes at a higher temperature than aluminium chloride is of no importance, for it will be found that amongst the members of the former series, with its difficultly fusible and volatilisable chlorides, many analogies exist for beryllium, not only in this but in many other respects.

Lastly, we subjoin a table showing the magnetic properties of the rare earths. Mr. Knut Ångström kindly undertook this research, employing a powerful electromagnet of Ruhmkorff, between the poles of which the oxides showed the following properties:—

Magnetic.		Diamagnetic.
Cr_2O_3		Be_2O_3
Fe_2O_3		Al_2O_3
Y_2O_3		Sc_2O_3 ?
Di_2O_3		In_2O_3
Er_2O_3		La_2O_3
Yb_2O_3		—
—		ZrO_2
CeO_2		ThO_2

III. "On the Absorption Spectra of Cobalt Salts." By W. J. RUSSELL, Ph.D., F.R.S., Treas. C.S., Lecturer on Chemistry at the Medical School, St. Bartholomew's Hospital. Received August 4, 1880.

(Abstract.)

The following investigation was commenced with Mr. Lockyer, and although he has been unable to continue the work, the author is indebted to him for much aid and many suggestions.

The cobalt salt first examined was the anhydrous chloride. In order to establish clearly its absorption spectrum, different samples of this salt were made by various processes. All, however, gave the same spectrum. The bromide of cobalt yields a similar spectrum, but its position is different, it is nearer to the red.